

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C11D 3/16, 3/43</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/36980</b> <b>(43) International Publication Date:</b> 9 October 1997 (09.10.97)
<b>(21) International Application Number:</b> PCT/US97/05191 <b>(22) International Filing Date:</b> 31 March 1997 (31.03.97)  <b>(30) Priority Data:</b> 08/626,402 2 April 1996 (02.04.96) US  <b>(71) Applicant:</b> S.C. JOHNSON & SON, INC. [US/US]; 1525 Howe Street, Racine, WI 53403-2236 (US).  <b>(72) Inventor:</b> NEUMILLER, Philip, J.; 4734 West Knollwood Drive, Racine, WI 53403 (US).  <b>(74) Agents:</b> BOZEK, Laura, L. et al.; Patent Section, S.C. Johnson & Son, Inc., 1525 Howe Street, Racine, WI 53403-2236 (US).		<b>(81) Designated States:</b> BR, CA, JP, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> ACIDIC CLEANING FORMULATION CONTAINING A SURFACE MODIFICATION AGENT AND METHOD OF APPLYING THE SAME  <b>(57) Abstract</b>  An acidic cleaning formulation containing a surface modification agent selected from a group consisting of a hydrolyzed trialkoxy silane or a hydrolyzable quaternary silane and a surfactant is disclosed. The cleaning formulation is stable, provides excellent cleaning efficacy and deposits a silane coating on the surfaces to which it is applied to leave a protective coating thereon. Also, disclosed is a method for applying the cleaning formulation to hard surfaces covered by water.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CJ	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LJ	Liechtenstein	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

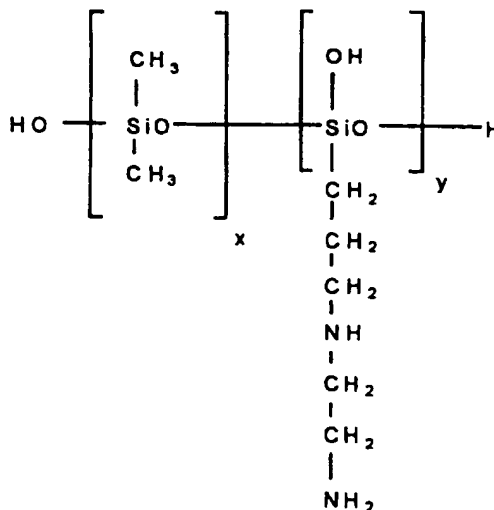
# ACIDIC CLEANING FORMULATION CONTAINING A SURFACE MODIFICATION AGENT AND METHOD OF APPLYING THE SAME

## 5 Technical Field

This invention relates to an acidic cleaning formulation containing a surface modification agent selected from the group consisting of a hydrolyzed trialkoxysilane and a hydrolyzable quaternary silane. The formulation is applied to hard surfaces to clean the surface and provide a uniform silane coating on the  
10 cleaned surface. The invention also relates to a method for applying the acidic cleaning formulation of this invention to hard surfaces covered by water.

## Background Art

It is known to apply silane cleaning solutions to surfaces to impart water  
15 repellency and provide a protective barrier on the treated surface. For example, U.S. Patent No. 4,948,531 discloses an aqueous cleaning composition comprising (a) one or two nonionic surfactants and an amphoteric surfactant as cleaning agents, (b) lecithin and an aminofunctional polydimethylsiloxane copolymer as protective barrier components, (c) one or two glycols as solvency and grease cutting agents,  
20 and (d) water. The disclosed aminofunctional polydimethylsiloxane copolymer has the formula:



- 2 -

and is available as Dow Corning 531 Fluid (Dow Corning Corporation, Midland, Michigan) which is a 50% solution in aliphatic solvents and isopropyl alcohol. This composition is said to clean a surface and simultaneously leave a protective barrier on the cleaned surface.

5 U.S. Patent No. 4,005,030 describes a detergent composition containing an organosilane and an anionic surfactant. The organosilane is said to attach to the hard surfaces to which the detergent composition is applied. U.S. Patent No. 4,005,025 describes a similar detergent composition containing an organosilane, a water-soluble surfactant and a source of alkalinity. This patent also discloses that  
10 the composition preferably contains an amine oxide. However, the composition is said to be unstable when the pH of the composition is not alkaline.

U.S. Patent No. 4,859,359 is directed to a hard surface cleaning and polishing composition comprising a solvent mixture of a glycol ether, a lower aliphatic alcohol, a hydrocarbon solvent and a minor amount of water together with  
15 an organic polysiloxane, a silane and a polycarboxylic chelating acid. The silane compound, which is said to promote the solubility of the other silicone compounds in the mixture, is represented by the formula:



20 wherein  $R^3$  is an alkyl radical containing one to three carbon atoms or phenyl and  $R^4$  is an alkyl radical containing one or two carbon atoms. The alkyl trialkoxysilanes are disclosed as preferable.

U.S. Patent 5,073,195 is directed to an aqueous solution of a water silane  
25 coupling agent, preferably an amino functional silane coupling agent, and an alkyltrialkoxysilane such as methyltrimethoxysilane or isobutyltrimethoxysilane. The composition is used to treat a surface to impart water repellency to that surface.

Alkoxysilanes are known to hydrolyze upon exposure to water to form  
30 reactive silanol groups. The silanol group may then condense with a reactive site on a treated surface. However, if the silanol group is available during storage it may

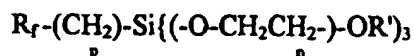
- 3 -

self-condense with other silanol groups to form an insoluble polymer. Hydrolysis of silanes in aqueous medium may be avoided by buffering the emulsions to a specific pH range such as disclosed in U.S. Patent No. 4,877,654. This patent describes a buffered aqueous silane emulsion containing a hydrolyzable silane that is

- 5 hydrolytically stable within a determined pH range, an emulsifier having an HLB value of from 1.5 to about 20, a buffering compound and water. However, a buffered composition restricted to a certain pH range can be particularly limiting to a formulator of cleaning compositions.

- PCT International Publication No. WO 92/14810 discloses that certain
- 10 organosilanes containing hydrolyzable groups, especially quaternary ammonium functional organosilanes, can form clear solutions in aqueous media which are stable over extended periods of time by including a water soluble organic, non-silicon quaternary ammonium compound along with nonionic, amphoteric, sarcosine anionic or certain cationic surfactants. The stabilization of hydrolyzable quaternary
- 15 silanes in the absence of a non-silicon quaternary ammonium compound is not disclosed or suggested. Moreover, the use of hydrolyzed organosilanes is not exemplified.

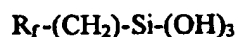
- PCT International Publication No. WO 95/23804 is directed to a hydrolyzed silane obtained by emulsifying a hydrolyzable alkoxysilane represented by the
- 20 formula:



- 25 wherein  $R_f$  is a perfluoroalkyl radical of 3 to 18 carbon atoms, each  $R'$  is independently an alkyl radical of 1 to 3 carbon atoms,  $p$  is 2 to 4 and  $n$  is 2 to 10, with an effective amount of an emulsifier of sufficiently high HLB value to simultaneously retain the hydrolyzable alkoxysilane compound in a substantially totally hydrolyzed state while inhibiting the self-condensation of the hydrolyzed
- 30 alkoxysilane. Suitable emulsifiers are said to include alkylbenzenesulfonates, linear alkyldiphenyletherdisulfonates, alpha-olefin sulfonates, ethoxylated alkyl alcohol

ethers, ethoxylated alkyl alcohol ether sulfates, ethoxylated alkylphenols, ethoxylated alkylphenol ether sulfates, ethoxylated perfluoroalkylalkanols, C<sub>8-18</sub> alkyltrimethylammonium salts, C<sub>8-18</sub> alkyldimethylammonium salts, ethoxylated C<sub>8-18</sub> amine salts, alpha-trimethylamino fatty acid betaines and perfluoroalkyl amphoteric surfactants of the type R-CH<sub>2</sub>CH(OR')CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub> (inner salt) where R' is H or acetyl, and quaternary salts of the type R-CH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH(OH)CH<sub>2</sub>N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>Cl<sup>-</sup>. According to PCT International Publication No. WO 95/23804, the alkoxysilanes are believed to be hydrolyzed to hydroxysilanes represented by the formula:

10



which do not substantially self-condense when the emulsifier is present.

A similar, but non-fluorinated, alkoxysilane aqueous emulsion is TLF-8291, available from E. I. Du Pont de Nemours and Company, Wilmington, Delaware. TLF-8291 is believed to contain hydrolyzed C<sub>18</sub>-alkyltrialkoxysilane (about 10% by weight of the emulsion) in combination with C<sub>8-18</sub> tetraalkylammonium chloride (about 30 to 40% by weight of the silane) in water. While the hydrolyzed trialkoxysilane aqueous emulsion appears stable as provided, simple dilution of the aqueous emulsion has been found to give a commercially unacceptable cleaning formulation due to poor cleaning efficacy and silane attachment to glass containers holding such a formulation.

Cleaning formulations containing hydrolyzable quaternary silanes or hydrolyzed trialkoxysilanes, such as TLF-8291, which are stable, avoid substantial silane attachment to glass storage containers, provide excellent cleaning, uniform surface deposition after wipe out, and excellent surface wetting and leveling would be highly desirable.

### Summary Of Invention

This invention relates to an acidic cleaning formulation for cleaning hard surfaces comprising: (a) a surface modification agent selected from the group consisting of (i) a hydrolyzed trialkoxysilane in an amount from about 0.00001 to about 10.0 percent by weight of the formulation and (ii) a hydrolyzable quaternary silane in an amount from about 0.00001 to about 10.0 percent by weight of the formulation; (b) a surfactant in an amount from about 0.00001 to about 10.0 percent by weight of the formulation, provided that if the surface modification agent is a hydrolyzable quaternary silane then the surfactant is not a quaternary ammonium compound or sulfobetaine; (c) at least one alcohol having 1 to 12 carbon atoms; and water. Preferably, the hydrolyzed trialkoxysilane is formed in an aqueous emulsion from a hydrolyzable trialkoxysilane compound emulsified in water with about 5 to 100 percent by weight of an emulsifier based on the weight of the hydrolyzable trialkoxysilane and the surfactant is different than the emulsifier. In this preferred embodiment, the emulsifier employed to emulsify the hydrolyzable trialkoxysilane must be in an amount effective to keep the hydrolyzable trialkoxysilane in a substantially totally hydrolyzed state while simultaneously inhibiting appreciable self-condensation of the silane in the aqueous emulsion. The formulation has a pH less than 7.0 which is generally attained by the addition of an acid. Preferably, the alcohol is a mono, di or tri hydric alcohol. The formulation may also include glycol ethers, solvents, fragrances and any other components well known to those skilled in the art of cleaning formulations.

Another embodiment of the present invention is directed to the above-described cleaning formulation having reduced autophobicity, *i.e.*, the tendency of the formulation to repel itself after application to a hard surface. It has been surprisingly discovered that the autophobicity of the formulations of the present invention can be reduced by the addition of a siloxane to the formulation. Such siloxanes include, for example, polydimethylsiloxane and derivative thereof.

Yet another embodiment of this invention is directed to a method of applying a surface modification agent to a surface covered by water by adding the

above-described acidic cleaning formulation to the water. It has been surprisingly discovered that the surface modification agent of the formulation of this invention attaches to and modifies the surface of substrates, such as glass, ceramic, fiberglass or porcelain, when applied to the water covering such a surface. It has further been  
5 discovered that such surface modification occurs even when relatively low levels of the surface modification agents are added to the water covering such surfaces. This method employing the acidic cleaning formulations of this invention may be advantageously employed to clean and protect surfaces covered by water, e.g. toilet bowls, with a minimal use of materials and effort.

10 The cleaning formulations of this invention are particularly useful for cleaning hard surfaces such as glass, mirrors, tile, ceramic and the like while providing the cleaned surface with a protective silane coating. The formulations of the invention are highly storage stable even when packaged in glass containers, effectively avoid substantial surface attachment of the active silane to the storage  
15 container, and thus preserve the active silane for attachment to treated surfaces.

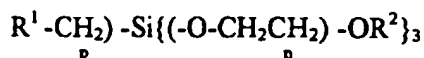
#### Modes For Carrying Out The Invention

This invention is directed to an acidic cleaning formulation which contains a  
20 surface modification agent selected from the group consisting of a hydrolyzed trialkoxysilane or a hydrolyzable quaternary silane in a stabilized formulation. The hydrolyzed trialkoxysilane or hydrolyzable quaternary silane are available for attachment to a surface treated with the aqueous acidic cleaning formulations to form a protective barrier which advantageously inhibits the deposition of soils and  
25 grease on the treated surface.

The hydrolyzed trialkoxysilane that may be employed in the formulation of this invention is derived from a hydrolyzable trialkoxysilane represented by the formula (I):



- 7 -



5 wherein  $R^1$  is selected from the group consisting of a perfluoroalkyl group of 3 to 18 carbon atoms or an alkyl group of 3 to 24 carbon atoms, and  $R^2$  is independently an alkyl group having 1 to 3 carbon atoms,  $p$  is 0 to 4 and  $n$  is 2 to 10. Preferably  $R^1$  is an alkyl group of 3 to 24 carbon atoms and  $p$  is O, most preferably  $R^1$  is an alkyl group having 18 carbon atoms and  $p$  is O.

10 The amount of hydrolyzable trialkoxysilane used in the aqueous emulsion is generally in the range from about 0.00001 to about 25.0 percent by weight of the aqueous emulsion, most preferably from about 0.00001 to about 10.0 percent by weight. Any amount of hydrolyzable trialkoxysilane may be employed in the aqueous emulsion so long as the emulsion is stable prior to its use in preparing the  
15 cleaning formulation of this invention.

The hydrolyzed trialkoxysilane may be readily prepared by one of ordinary skill in the art by emulsifying the hydrolyzable trialkoxysilane of formula I in water to form an aqueous emulsion with an emulsifier of sufficiently high HLB value to simultaneously retain the hydrolyzable trialkoxysilane compound in a substantial  
20 totally hydrolyzed state and inhibit the hydrolyzed trialkoxysilane compound from appreciable self-condensation. The preparation of aqueous emulsions of hydrolyzed trialkoxysilanes are shown, for example, in PCT International Publication No. WP 95/23804, the disclosure of which is incorporated by reference herein. It may also be possible to form the hydrolyzed trialkoxysilane insitu by the admixture of a  
25 hydrolyzable trialkoxysilane with the other components of the formulation of this invention.

If present, the emulsifier generally has an HLB ("The HLB System" published by ICI America's Inc., Wilmington, Delaware) value greater than 12. However, when a non-fluorinated trialkoxysilane is employed, then preferably the  
30 HLB value of the emulsifier is greater than 16, more preferably greater than 18.

- 8 -

Compatible emulsifiers may be used in admixture as long as each meets the above-defined HLB requirements.

Emulsifiers that are preferred for use with a non-fluorinated trialkoxysilane include, without limitation, C<sub>8-18</sub> alkyltrimethylammonium quaternary salts, alkali metal alkylbenzene-sulfonates, linear alkyl diphenyletherdisulfonates, alpha-olefin sulfonates, alkyl and alkylether sulfates, C<sub>12-18</sub> alkyl dimethylammonium salts, polyethoxylated C<sub>12-18</sub> alkyl ammonium salts and highly ethoxylated alkyl and aryl alcohols. Such emulsifiers include, for example, hexadecyltrimethylammonium chloride, the sodium salt of C<sub>14-16</sub> alpha olefin sulfonate, octadecylamine-60 E.O. and octadecyldimethylammonium chloride.

A particularly preferred emulsifier, particularly for use with a hydrolyzed trialkoxysilane where R<sup>1</sup> is a C<sub>12</sub> to C<sub>24</sub> alkyl group, is an ethoxylated C<sub>8-18</sub> amine salt, more preferably tetraalkylammonium chloride, most preferably, having predominantly C<sub>16</sub>-alkyl groups.

Generally, about 5 to 100 percent by weight of an emulsifier based on the weight of the hydrolyzable alkoxy silane is employed in the aqueous emulsion. When R<sup>1</sup> is a alkyl group of 3 to 24 carbon atoms then preferably the emulsifier is present in an amount of 10 to 50% based on the weight of the silane, most preferably 30 to 40%. A particularly preferred commercially available hydrolyzed trialkoxysilane emulsion is previously described TLF-8291, available from E.I. Du Pont de Nemours and Company (Wilmington, Delaware).

Typically, the aqueous emulsion containing the hydrolyzed trialkoxysilane and emulsifier is present in the cleaning formulation in an amount from about 0.0001 to about 1.0 percent by weight of the cleaning formulation, most preferably from about 0.0001 to about 0.1 percent by weight. The amount of aqueous emulsion used in the cleaning formulation will, of course, depend on the concentration of the hydrolyzed trialkoxysilane in the aqueous emulsion. Thus, any amount of aqueous emulsion may be employed that provides an effective amount of hydrolyzed trialkoxysilane in the cleaning formulation to change the hydrophobicity of a treated surface by surface attachment of the hydrolyzed trialkoxysilane.

- 9 -

Not wanting to be bound by any theory, but so as to provide a full disclosure, it is believed that the hydrolyzed trialkoxysilane is represented by (i) the formula (II):

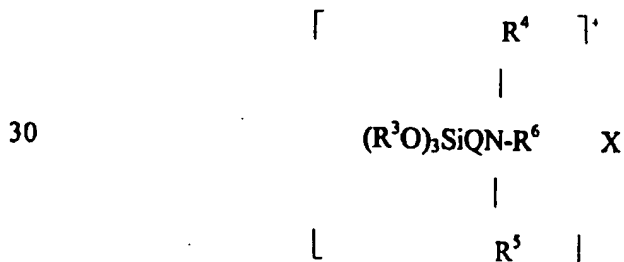


wherein  $R^1$  and  $p$  are the same as described for formula I, (ii) by oligomers of formula II or (iii) mixtures thereof. The hydrolyzed trialkoxysilane may form  
 10 oligomers by the self-condensation of the silanol groups of two or more hydrolyzed trialkoxysilanes so long as the oligomer remains soluble in the aqueous emulsion.

Again, without wishing to be bound by any theory, it is believed that the hydrolyzed trialkoxysilane forms a micelle in conjunction with the emulsifier and that after this aqueous emulsion is diluted into a cleaning formulation the  
 15 hydrolyzed trialkoxysilane is further protected and stabilized by the addition of the surfactants used in this invention in combination with at least one alcohol having 1-12 carbon atoms and by adjusting the pH of the formulation to an acidic pH. This cleaning formulation allows delivery of the silane to a surface with excellent surface orientation after evaporation of the aqueous carrier. In addition, it is believed that  
 20 the surfactant inhibits the silane, while in solution, from substantial surface attachment to the storage container and thus preserves the reactive silane for attachment to the treated surface upon application.

The hydrolyzable quaternary silane that may be employed in the formulation of this invention is represented by the formula:

25



wherein  $R^3$  is a hydrolyzable lower alkyl group having 1 to 6 carbon atoms,  $R^4$ ,  $R^5$  and  $R^6$  are each independently alkyl groups having 1 to 24 carbon atoms, Q is an alkylene radical having 1 to 6 carbon atoms and X is an alkali metal. Particularly preferred hydrolyzable quaternary silanes include, without limitation, 3-

5 (trimethoxysilyl) propyldimethyloctadecylammonium chloride (available as Dow Corning Q9-6346 Quaternary Silane from Dow Corning Corp., Midland, Michigan) and 3-(trimethoxysilylpropyl) didecylmethylammonium chloride (available as Y-11724 Requat Antimicrobial Liquid from Sanitized, Inc., New Preston, Connecticut).

10 When used, the amount of hydrolyzable quaternary silane present in the formulation will range from about 0.00001 to a about 20.0 percent by weight of the formulation, preferably from about 0.00001 to about 10.0 percent by weight of the formulations.

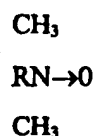
The surfactants employed in the formulation of this invention are selected  
15 from the group consisting of: nonionic surfactants such as, for example, linear ethoxylated alcohols (e.g., Neodol® 25-7 (C12-C15 alcohol, EO 7), Neodol® 23-6.5 (C12-C13 alcohol, EO 6.5), Neodol® 1-7 (C12-C13 alcohol, EO 7), Neodol® 25-9 (C12-C15 alcohol, EO 9), Neodol® 45-7 (C14-C15 alcohol, EO 7), or Neodol® 91-6 available from Shell Chemical Co., Houston, Texas, Surfonic® L12-  
20 8 (C11-C12 alcohol, EO 8), Surfonic® L12-6 (C11-C12 alcohol, EO 6), Surfonic® L24-6.5 (C12-C14 alcohol EO 6.5), Surfonic® L24-7 (C12-C14 alcohol, EO 7), Surfonic® L24-9 (C12-C14 alcohol, EO 9) or Surfonic® 108-83-5 available from Huntsman Corp., Austin, Texas), alcohol ethoxy carboxylic acids (e.g., Neodox® 23-7, Neodox® 25-6 or Neodox® 45-7) or other nonionic surfactants (e.g., Brij®  
25 76 (polyoxyethylene (20) stearyl ether) or Brij® 97 (polyoxyethylene (10) oleyl ether) available from ICI Americas, Wilmington, Delaware, Pluronic® L-44 (block copolymers of propylene/ethylene oxide) available from BASF, Parsippany, New Jersey, Berol® 223 (fatty amine ethoxylate) available from Berol Nobel, Stratford, Connecticut, and Zonyl® FS-300 (fluoroalkyl alcohol substituted monoether with  
30 polyethylene glycol) available from E.I. Du Pont de Nemours and Co., Wilmington,

Delaware; amphoterics, such as betaines (e.g., Emcol® CC37-18 available from Witco, Houston, Texas, Lonzaine® C or Lonzaine® CO (cocamidopropylbetaines) available from Lonza Inc., Fairlawn, N.J., Mirataine® BB (lauramidopropyl betaine), Mirataine® CB, or Mirataine® Bet C-30 (cocamidopropyl betaines) 5 available from Rhone-Poulenc, Cranbury, New Jersey, Monateric® CAB available from Mona Chemical Co., Paterson, New Jersey and Witco DP 5C-5298-53 (C10 dimethyl betaine) or Witco DP SC-5298-49 (C8 dimethyl betaine) available from Witco), sultaines (e.g., Mirataine® ASC (alkyletherhydroxypropylsultaine) or Mirataine® CBS (cocoamidopropylhydroxysultaine) available from Rhone Poulenc, 10 Lonzaine® CS or Lonzaine® JS (cocoamidopropylhydroxysultaines) available from Lonza Inc., Fairlawn, N.J. and Rewoteric® AM CAS (cocoamidopropylhydroxysultaine) available from Witco), or imidazoline amphoterics (e.g., Amphoterger® W (cocoamphoacetate), Amphoterger® W-2 (cocoamphodiacetate), Amphoterger® K (cocoamphopropionate), Amphoterger® K- 15 2 (cocoamphodipropionate), Amphoterger® L (lauroamphodiacetate), Amphoterger® J-2 or Amphoterger® KJ-2 (capryloamphodipropionate) available from Lonza, Rewoteric® AM V (caprylic glycinate), Rewoteric® AM-KSF (cocoamphopropionate) or Rewoteric® AM 2L (lauroamphodiacetate) available from Witco, Phosphoteric® T-C6 (dicarboxyethyl phosphoethyl imidazoline), 20 Monateric® Cy-Na, or Monateric® LF-Na available from Mona, and Miranol® C2M (cocoamphodiacetate), Miranol® J2M (capryloamphodiacetate), Miranol® JAS (imidazoline amphoteric) available from Rhone-Poulenc); and cationic surfactants such as amine oxides (e.g., Barlox® LF, Barlox® C, Barlox® 105, Barlox® 12, Barlox® 16S, or Barlox® 18S available from Lonza, Rhodamox® LO 25 or Rhodamox® CO available from Rhone-Poulenc and Varox® 305 or Varox® 743 available from Witco), and quaternary cationic surfactants (e.g., Bardec® 208M or Barquat® 42802 available from Lonza and BTC 835 available from Stephan, Co., Northfield, Illinois), or dialkoxyl alkyl quaternaries (e.g., Variquat® 66, Variquat® K-1215, Adogen® 444, Adogen® 461 or Adogen® 462 available 30 from Witco).

If the surface modification agent is a hydrolyzable quaternary silane then the surfactant is not a quaternary ammonium compound or sulfobetaine. The preferred surfactants for use with the hydrolyzable quaternary silanes are amphoteric betaines or amine oxides. For a trialkoxysilane surface modification agent, the preferred  
 5 surfactants employed in the cleaning formulation of this invention include amine oxides, amphoteric sultaines, amphoteric betaines and quaternary cationic surfactants, most preferably amine oxides such as Lonza Barlox® 12 and amphoteric betaines such as Lonzane® CO.

The particularly preferred amine oxides are represented by the formula:

10



15

wherein R is a C<sub>8</sub> to C<sub>16</sub> alkyl group. Most preferably R is a C<sub>12</sub> alkyl group.

If the formulation contains a trialkoxysilane, then the surfactant employed in the formulation of this invention will differ from the emulsifier described above. At least one surfactant must be present, although, it may be preferable to employ more  
 20 than one surfactant.

Generally, a surfactant or mixture of surfactants will be present in the formulation in an amount from about 0.00001 to about 10 percent by weight of the formulation, more preferably in an amount from about 0.0001 to about 5 percent by weight of the formulation and most preferably in an amount from about 0.0001 to  
 25 about 3 percent by weight of the formulation. However, any amount of surfactant may be employed that provides a formulation that contains a stabilized hydrolyzed trialkoxysilane or a stabilized hydrolyzable quaternary silane and which has good cleaning properties.

The formulation of this invention contains at least one alcohol having 1 to  
 30 12 carbon atoms that are preferably selected from mono, di and tri hydric alcohols.

Such mono, di and tri hydric alcohols include, for example, ethanol, propanol, hexanol, isopropanol, N-pentanol, propylene glycol, glycerin, 2-pentanol, 3-pentanol, 2-butanol, diethylene glycol, Neodol® 91 (C<sub>9</sub> - C<sub>11</sub> primary alcohol), Neodol® 1 (C<sub>11</sub> primary alcohol) and decyl alcohol. Generally, the concentration of  
5 the mono, di or tri hydric alcohols in the formulation is in a range from about 0.00001 to about 5.0 percent by weight of the formulation. The amount of alcohol employed in the formulation of this invention should be maintained below that amount which would cause substantial alkylation of the hydrolyzed trialkoxysilane.

Besides the alcohols described above, the formulations of this invention may  
10 also include other solvents, such as glycol ethers, to assist in cleaning the treated surface. Typical glycol ethers include, without limitation Dowanol® EB, (ethylene glycol n-butyl ether), Dowanol® DB (diethylene glycol n-butyl ether), Dowanol® PnB (propylene glycol n-butyl ether), Dowanol® DPnB (dipropylene glycol n-butyl ether), Dowanol® PPH (propylene glycol phenyl ether), Dowanol® PMA  
15 (propylene glycol methyl ether acetate), Dowanol® EPH (ethylene glycol phenyl ether), Dowanol® DPMA (dipropylene glycol methyl ether acetate), Dowanol® DPM (dipropylene glycol methyl ether), Dowanol® PnP (propylene glycol n-propyl ether), Witco® DM-55 (polyethylene glycol dimethyl ether) and the like. If employed, the glycol ethers are generally present in the formulation in an amount  
20 from about 0.1 to about 6.0 percent by weight of the formulation.

The formulations of this invention typically include an acid to ensure that the pH of the formulation is less than 7, and preferably from about 0.5 to about 6.95, most preferably about 0.75 to about 5. Generally, such an acid is present in an amount from about 0.00001 to about 7.5 percent by weight of the formulation.  
25 Exemplary acids include, without limitation, glycolic acid, lactic acid, acetic acid, sulfamic acid, citric acid and gluconic acid. Glycolic acid and lactic acid are preferred.

Additional adjuvants which may be employed in the formulations of this invention include fragrances, colorants and the like. The use of such adjuvants is  
30 well known to those of ordinary skill in the art.

The preparation of the cleaning formulations will vary depending on the surface modification agent employed. For example, if the surface modification agent is a quaternary silane then it is preferred to first add the surfactant to water followed by the addition of the agent. Thereafter, any solvents, bases or other  
 5 adjuvants may be added to the formulations. It has been surprisingly discovered that the activity of the hydrolyzable quaternary silane is better preserved when using the method of preparation described above, while the addition of the hydrolyzable quaternary silane after mixing the other formulation components may result in a loss of activity for the surface modification agent. On the other hand, when employing a  
 10 hydrolyzed trialkoxysilane, it is most preferable to add the silane last to the completed formula.

In yet another embodiment of this invention, a siloxane is added to the above described cleaning formulation to reduce the autophobicity of those formulations. The siloxanes that may be employed include polydimethyl- siloxane  
 15 and derivatives thereof. Such derivatives may include, for example, polyalkylene oxide-modified polydimethylsiloxanes represented by the formula



20

PE

wherein PE is represented by  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{EO})_m(\text{PO})_n\text{Z}$  wherein EO is ethyleneoxy, PO is 1,2-propyleneoxy and Z is hydrogen or a lower alkyl group, or

25



wherein PE' is represented by  $-(\text{EO})_m(\text{PO})_n\text{R}$  wherein EO and PO are the same as described above and R is a lower alkyl group.

Other siloxanes which may be useful for reducing autophobicity include  
 30 aromatic substituted siloxanes such as diphenyldimethylsiloxane copolymers, phenylmethylsiloxane polymers and methyl (propyl hydroxide, ethoxylated) bis (trimethylsiloxy) silane (Dow Corning® Q2-5211, available from Dow Corning, Midland, Michigan).



If present, the siloxane is employed in an amount effective to reduce the autophobicity of the cleaning formula. Generally, about 0.00001 to about 0.5 percent of siloxane by weight of the formulation may be added to inhibit autophobicity. However, any amount of siloxane that is effective to inhibit autophobicity is encompassed by the present invention.

This invention is also directed to a method of applying a surface modification agent to a hard surface, such as glass, ceramic, fiberglass or porcelain, that is covered by water. The above-described acidic cleaning formulation is added directly to the water in an amount effective to modify the surface covered by the water through attachment of the surface modification agent, i.e., the silane, to that surface.

Without being bound to theory, it is believed that the silane contained in the formulation of this invention has a preferred orientation for liquid/air or liquid/solid surfaces. After the acidic cleaning formulation is introduced to the water, it is believed that the surface modification agent, i.e., the hydrolyzed trialkoxysilane or hydrolyzable quaternary silane, is no longer stabilized to inhibit surface attachment and that the reactive silane migrates to the liquid/solid interface and adheres to the surface. It has been surprisingly discovered that surface modification can be obtained with as little as 0.1 ppm to 100 ppm of surface modification agent in the water.

The method of this invention can be readily practiced, for example, by the addition of an effective amount of the acidic cleaning formulation to water contacting the surface which is to be treated. The amount of acidic cleaning formulation that is added to the water is dependent on the concentration of surface modification agent in the formulation, the amount of water contacting the surface and the surface area that is to be coated. Generally, the amount of acidic cleaning formulation added to the water is an amount that will provide at least about 0.1 ppm of surface modification agent in the water. The acidic cleaning formulation may be added to the water in any manner desired, such as by direct application or by a slow release mechanism, e.g., a toilet bowl tank dispenser.

The Examples which follow are intended as an illustration of certain preferred embodiments of the invention, and no limitation of the invention is implied.

5

Example 1

A cleaning formulation was prepared containing the following components (as used herein % w/w means the percent weight of the component based on the weight of the formulation unless otherwise specified):

Components	% w/w
Lonza® CO (amphoteric betaine) <sup>1</sup>	3.000
Glycerin	0.100
Isopropyl Alcohol	1.000
Deionized Water	88.100
Lactic Acid	6.800
TLF-8291 <sup>2</sup>	<u>1.000</u>
	100.000
<sup>1</sup> C <sub>6</sub> -C <sub>18</sub> amphoteric betaine	
<sup>2</sup> 10% C <sub>18</sub> -alkyltrialkoxyl silane with C <sub>16</sub> -tetraalkylammonium chloride (30 to 40% based on the silane) in an aqueous emulsion available from E.I. Du Pont de Nemours & Co., Wilmington, Delaware	

10

Example 2

A cleaning formulation was prepared in a manner similar to Example 1, except the surface modification agent was Dow Corning Q9-6346 (72%) available from Dow Corning, Midland, Michigan.

15

Example 3

The cleaning formulation was prepared in a manner similar to Example 1, except the surface modification agent was Requat 2-C10, available from Sanitized Inc., New Preston, Connecticut.

5

Example 4

A cleaning composition was prepared having the following components:

Components	% w/w
Lonza Lonzaine® CO <sup>1</sup>	3.000
Shell Neodox® 25-6 <sup>2</sup>	2.000
Shell Neodol® 25-7 <sup>3</sup>	0.500
Glycerin	0.300
Isopropyl Alcohol	1.000
Witco® DM 55 <sup>4</sup>	1.000
Dow Triad <sup>5</sup>	1.000
Fragrance	0.150
Dow Corning® Q2-5211 <sup>6</sup>	0.010
Deionized Water	84.040
Citric Acid	3.000
Sulfamic Acid 98%	3.000
TLF-8291	1.000
	100.000
<sup>1</sup> C <sub>6</sub> -C <sub>18</sub> amphoteric betaine (cocamidopropyl betaine) <sup>2</sup> alcohol ethoxycarboxylic acid <sup>3</sup> C <sub>12</sub> -C <sub>15</sub> linear ethoxylated alcohol <sup>4</sup> polyethylene glycol dimethyl ether <sup>5</sup> Equal parts of Dowanol® PnP, DPM and PnB <sup>6</sup> siloxane	

This formulation was found to clean (rust and manganese) stains on porcelain and to deposit the active silane under water. The pH of the solution was 1.05.

Example 5A

A cleaning formulation having the following components was prepared.

Components	% w/w
Neodol® 25-7	4.000
Lonzaine® CO	3.000
Dow Triad	1.950
Glycerin	0.140
Isopropyl Alcohol	3.000
Isopar E <sup>1</sup>	1.000
Witco® DM55	4.000
Fragrance	0.250
Deionized Water	75.350
Dow Corning® Q2-5211	0.010
Lactic Acid	6.800
TLF-8291	0.500
<sup>1</sup> Isoparaffinic Hydrocarbon	

This cleaning formulation had a pH of about 2.

Example 5B

A cleaning formulation having the following components was prepared:

Components	% w/w
Deionized Water	82.795
Lactic Acid	5.500
Lonzaine® CO	2.250
Neodol®25-7	2.850
Witco® DM 55	1.000
Glycerin	0.100
Isopropyl Alcohol	4.000
Isopar E	0.900
Dow Corning® Q2-5211	0.005
Fragrance	0.200
TLF-8291	0.400

This cleaning formulation provided excellent cleaning efficacy and stability.

Example 6

A cleaning formulation having the following components was prepared.

Components	% w/w
Barlox LF <sup>1</sup>	0.250
Isopropyl Alcohol	3.000
Neodox 25-6 <sup>2</sup>	0.100
Dow Triad	1.000
Fragrance	0.050
n-hexanol	0.075
Deionized Water	94.965
Dow Corning® Q2-5211	0.010
Lactic Acid (85%)	0.200
TLF-8291	0.350
<sup>1</sup> Amine oxide	
<sup>2</sup> C <sub>12</sub> -C <sub>15</sub> alcohol ethoxycarboxylic acid	

Example 7

A cleaning formulation having the following components was prepared.

Components	% w/w
Lonza Barlox® 12 (amine oxide)	0.500
Lonzaine® CO (amphoteric surfactant)	0.500
Propylene Glycol	1.500
Isopropyl Alcohol	2.000
Dowanol® PnP	1.000
Dowanol® PnB	1.000
Dowanol® DPM	1.000
Fragrance	0.060
n-hexanol	0.200
Deionized Water	84.063
Glycolic Acid (70%)	7.170
TLF-8291	1.000
Colorant	0.007

5 The pH of the resulting formulation was 2.21.

Examples 8-9

Cleaning formulations were prepared having substantially the same composition as Example 7, except that the amine oxide was Lonza Barlox® LF and

10 Lonza Barlox® 10-S, respectively. The cleaning formulation of Example 9 had a pH of 2.21.

Examples 10-29

Cleaning formulations were prepared having substantially the same composition of Example 7, except that the Lonzaine® CO amphoteric surfactant 5 was replaced with the one of the amphoteric surfactants described below.

Example	Amphoteric Surfactant	pH
10	Lonzaine® C	2.27
11	Mirataine® BB	2.21
12	DP SC-5298-49	2.19
13	DP SC-5298-53	2.30
14	Lonzaine® CS	2.20
15	Lonzaine® JS	2.13
16	Mirataine® ACS	2.18
17	Mirataine® CBS	2.25
18	Rewoteric® AM CAS	2.28
19	Amphoterge® K	2.32
20	Amphoterge® K-2	2.23
21	Amphoterge® KJ-2	2.90
22	Amphoterge® L-Special	2.20
23	Amphoterge® W	2.27
24	Amphoterge® W-2	2.32
25	Miranol® C2M Conc. NP	2.24
26	Miranol® J2M Conc.	2.18
27	Rewoteric® Am KSF-40	2.29
28	Rewoteric® AMV	2.34
29	Rewoteric® AM 2L-40	2.34



Examples 30-41

Cleaning formulations were prepared having substantially the same composition as Example 7, except the Lonzaine® CO amphoteric surfactant was replaced by one of the nonionic surfactants described below:

Example	Nonionic surfactants	pH
30	Zonyl® FS 300	2.34
31	Neodox® 25-6	2.37
32	Surfonic® L 24-7	2.42
33	Neodox® 45-7	2.31
34	Pluronic® L-44	2.41
35	Surfonic® L 12-8	2.37
36	Neodol® 45-7	2.25
37	Neodol 25-7	2.35
38	Neodol® 23-6.5	2.24
39	Surfonic® L 12-6	2.37
40	Berol® 223	2.27
41	Neodol® 1-7	2.37

Examples 42-49

Cleaning formulations were prepared having substantially the same composition as Example 7, except the mixture of glycol ethers (PnP, PnB and DPM) were replaced by an identical amount of the glycol ethers described below.

Example	Glycol ether	pH
42	DB (diethylene glycol n-butyl ether)	2.33
43	PnB (propylene glycol n-butyl ether)	-
44	DPnB (dipropylene glycol n-butyl ether)	-
45	PPh (propylene glycol phenyl ether)	-
46	DPM (dipropylene glycol methyl ether)	2.37
47	PnP (propylene glycol n-propyl ether)	2.31
48	Witco DM-55 (polyethylene glycol dimethyl ether)	2.35
49	EB (ethylene glycol n-butyl ether)	2.25

Examples 50-55

Cleaning formulations were prepared having substantially the same components as Example 7, except the n-hexanol was replaced by the alcohols listed below.

Example	Alcohol	pH
50	ethanol	2.30
51	propanol	2.02
52	pentanol	2.26
53	glycerin	2.28
54	2-pentanol	2.32
55	diethylene glycol	2.32

Examples 56-57

Two cleaning formulations were prepared having a composition similar to Example 7, except the isopropanol was replaced by ethanol and propanol, 5 respectively. Examples 56 and 57 had a pH of 2.27 and 2.30, respectively.

Examples 58-62

Cleaning formulations were prepared having a composition similar to Example 7, except that the glycolic acid was replaced by the following acids in the 10 amounts set forth below.

Example	Acid	% w/w	pH
58	Lactic Acid (80%)	6.274	2.30
59	Citric Acid (99.5%)	5.044	2.24
60	Sulfamic Acid (98%)	1.000	1.42
61	Gluconic Acid (50%)	10.038	2.82
62	Acetic Acid (30%)	6.670	3.39

Examples 63-64

Two cleaning formulations were prepared having a composition similar to Example 7, except the amine oxide (Lonza Barlox® 12) was replaced by Lonza 15 Barlox® 16-S and Lonza Barlox® 18-S, respectively. Examples 63 and 64 had a pH of 2.20 and 2.32, respectively.

Example 65

A cleaning formulation having the following components was prepared.

5

Components	% w/w
Shell Neodol® 25-7	4.000
Lonzaine® CO	3.000
Dowanol® DPM	0.650
Dowanol® PnB	0.650
Dowanol® PnP	0.650
Isopropyl Alcohol	1.000
Witco DM-55	5.000
Deionized Water	77.250
Lactic Acid (88%)	6.800
TLF - 8291	1.000

The formulation had a pH of 2.30.

Examples 66-86

Cleaning formulations were prepared having a composition similar to Example 65, except the surfactant Lonzaine® CO was replaced by the following 5 surfactants in the amounts set forth below.

Examples	Surfactant	% w/w	pH
66	Lonzaine® C	3.000	2.25
67	Mirataine® BB	3.500	2.29
68	DP SC-5298-49	2.941	2.38
69	DP SC-5298-53	2.830	2.34
70	Lonzaine® CS	2.100	2.14
71	Mirataine® ASC	2.442	2.08
72	Lonzaine® JS	2.143	2.16
73	Mirataine® CBS	2.386	2.14
74	Rewoteric® AM CAS-15U	2.100	2.17
75	Amphoterge® K	2.838	2.84
76	Amphoterge® K-2	2.625	2.85
77	Amphoterge® KJ-2	2.625	2.90
78	Amphoterge® L-Special	2.838	2.56
79	Amphoterge® W	2.283	2.60
80	Amphoterge® W-2	2.100	2.55
81	Miranol® C2M Conc. NP	2.763	2.61
82	Miranol® J2M Conc.	2.763	2.67
83	Rewoteric® AM KSF	2.625	2.86
84	Rewoteric® AM V	3.000	2.61
85	Rewoteric® AM2L	2.100	2.56
86	Mona Phosphoteric T-C6 (40%)	2.625	2.78

Note: Any difference in percent weight of the surfactant compound to that used in Example 65 was offset by the amount of deionized water used.

Examples 87-97

Cleaning formulations were prepared having a composition similar to Example 65, except the nonionic surfactant Shell Neodol® 25-7 was replaced by  
5 the following surfactants in the amounts set forth below.

Example	Surfactant	% w/w	pH
87	Neodol® 1-7	4.000	2.35
88	Neodol® 23-6.5	4.000	2.37
89	Neodol® 25-7	4.000	-
90	Neodol® 45-7	4.000	2.37
91	Surfonic® L12-8	4.000	2.28
92	Surfonic® L12-6	4.000	2.38
93	Surfonic® L24-7	4.000	2.38
94	Neodox® 25-6	4.444	2.49
95	Neodox® 45-7	4.444	2.35
96	Pluronic® L44	4.000	2.38
97	Berol® 223	4.000	2.47

Note: Any difference in percent weight of the surfactant compared to that used in Example 65 was offset by the amount of deionized water used

Example 98

A cleaning formulation was prepared having a composition similar to Example 65, except 0.25% w/w of Zonyl® FS-300 (fluoroalkyl alcohol substituted  
10 monether with polyethylene glycol available from E.I. Du Pont de Nemours & Co., Wilmington, Delaware) was added to the formulation. The formulation had a pH of 2.41.

Examples 99-106

Cleaning formulations were prepared having a composition similar to Example 65, except the glycol ethers (DPM, PnB, PnP and Witco DM-55) were replaced by 6.95% w/w of the following glycol ethers.

Example	Glycol ether	pH
99	Dowanol® EB (ethylene glycol n-butyl ether)	2.33
100	Dowanol® DB (diethylene glycol n-butyl ether)	2.44
101	Dowanol® PnB (propylene glycol n-butyl ether)	-
102	Dowanol® DPnB (dipropylene glycol n-butyl ether)	-
103	Dowanol® PPh (propylene glycol phenyl ether)	-
104	Dowanol® DPM (dipropylene glycol methyl ether)	2.44
105	Dowanol PnP (propylene glycol n-propyl ether)	2.46
106	Witco Varonic® DM-55 (polyethylene glycol dimethyl ether)	2.45

5

Examples 107-114

Cleaning formulations were prepared having a composition similar to Example 65, except the isopropanol was replaced by one of the following alcohols.

Example	Alcohol	pH
107	diethylene glycol	2.23
108	ethanol	2.26
109	glycerin	2.26
110	hexanol	2.28
111	pentanol	2.30
112	2-pentanol	2.31
113	propanol	2.33
114	propylene glycol	2.34

Examples 115-119

Cleaning formulations were prepared having a composition similar to Example 65, except the lactic acid was replaced by the following acids in the amounts set forth below.

Example	Acid	% w/w	pH
115	Glycolic acid	8.260	1.96
116	Gluconic acid (40-50%)	12.840	2.35
117	Citric acid (99.5+%)	5.780	1.93
118	Acetic acid (30%)	6.670	2.94
119	Sulfamic acid (98%)	0.500	1.63

5

Examples 120-121

Two cleaning formulations were prepared having compositions similar to Example 65, with the exceptions that Shell Neodol® 25-7 was replaced in both compositions by Surfonic® L12-8, and Lonzaine® CO was replaced by 2.625% w/w of Rewoteric® Am KSF-40 and Mona Phosphoteric® T-C6, respectively. Example 121 had a pH of 2.40.

10



Example 122

A cleaning formulation having the following components was prepared.

5

Example	% w/w
Surfonic® L12-8	4.000
Lonza Lonzaine® CO	3.000
Dowanol® DPM	6.950
Isopropanol	1.000
Deionized Water°	77.250
Lactic acid (88%)	6.800
TLF-8291	1.000

The formulation had a pH of 2.10.

Stability Testing

10

Two ounce samples of each formula were placed in a 100°F. (about 38° C.) oven. Each sample was visually monitored for up to a month. The results of these tests are set forth in Table 1. The preferred formulations of this invention remained clear, only slightly cloudy or swirly after two weeks to a month of observation.

15

Hydrophobicity Testing

Hydrophobicity of each formula was measured using a water drop test. This test measures how well a formulation exhibits sheeting of water. The test was  
20 conducted by first cleaning a mirror plate (12 in<sup>2</sup> (about 77 cm<sup>2</sup>) Mirror Model #P1212-NT, Monarch Mirror Co.) with HPLC grade acetone and a paper towel. Next, the mirror was rinsed with deionized water and blown dry. The mirror was then divided into 6 equivalent sections and about 0.15 to 0.25 g of a formula was applied to a section and wiped completely dry with half of a paper towel. After  
25 waiting one half hour, a pipette was used to deliver five drops of room temperature

tap water to each section and to a control section, i.e., a section of the mirror to which a formula was not applied. After 5 minutes each drop's diameter was measured parallel to the base of the mirror. An average drop size was calculated for each formula and the control.

- 5        The average drop size for the controls was 0.79 cm. The preferred formulas of this invention exhibited an improvement over the control. The results of the water drop test are set forth in Table 1.

#### Sliding Drop Test

10

The sliding drop test, which quantifies how a droplet flows or wets an inclined surface, was conducted on several of the formulations of this invention. The test was conducted on a 6 in<sup>2</sup> (about 15 cm<sup>2</sup>) glazed ceramic tile (Tilepak Glossy White CC-100), which was first cleaned with warm tap water and wiped  
15 dry. Each tile was treated with an equivalent amount of formulation (two to ten drops) and wiped dry. After ten minutes, a ceramic tile was placed on an incline and a Gilson Pipetman was used to dispense a 50 µL drop on each tile. The trail left on the tile was observed and rated on a scale of 0-5 as follows:

- 20 0 - indicates a continuous even trail the same width as the drop;  
1 - indicates a continuous trail narrower than the drop;  
2 - indicates a trail that is occasionally broken and narrower than the drop;  
3 - indicates a trail with only half the trail wetted;  
3.5 - indicates that elongated drops cover a quarter of the trail;  
25 4 - indicates that spherical drops cover a quarter of the trail;  
4.5 - indicates that the trail consists of only a few scattered spherical drops; and  
5 - indicates the drop rolls off the tile leaving no trail.

The results of this test are set forth in Table 2.

### Cleaning Tests

A cotton swab cleaning test was also utilized to test the cleaning efficacy of the formulations of this invention, versus interior soil, shell soil and beef tallow.

- 5        Interior soil was prepared by adding and melting together 0.5g of synthetic sebum, 0.5g of mineral oil, and 0.5g clay, followed by the addition of 98.5g of 1,1,1-trichloroethane. (Synthetic sebum consists of: 10% palmitic acid; 5% stearic acid; 15% coconut oil; 10% paraffin wax; 15% cetyl esters wax; 20% olive oil; 5% squalene; 5% cholesterol; 10% oleic acid; and 5% linoleic acid which are added
- 10 together and heated over low heat in order to melt the solids and form a homogeneous mixture.) Shell soil consists of 40 parts Metallic Brown Oxide (Pfizer B-3881); 24 parts Kerosene (deodorized); 24 parts Shell sol 340; 2 parts White Mineral Oil; 2 parts Shell Tellus 27; and 2 parts Hydrogenated Vegetable Oil (Crisco). The Shell soil was prepared by dissolving vegetable shortening (Crisco) in
- 15 kerosene and Shell Sol 340. Next, mineral oil, Shell Tellus 27 and pigment were added followed by agitating continuously for two hours.

- A mirror plate, like that employed in the hydrophobicity test, was cleaned with Classical EB Windex® and thoroughly dried with a paper towel. The soils were applied to the mirrors. After 24 hours, a cotton swab was dipped into the
- 20 formulations and wiped horizontally in a constant motion ten cycle pattern, about one inch (2.54 cm) long, with a constant pressure. After the cleaned areas were dry, the effectiveness of each formula was rated on a scale of one to ten, with one representing no soil removal. The results of the cleaning tests on the formulations of this invention are set forth in Table 1.

Table 1

Ex.	Drop Tests	Cleaning Test			Appearance at 100°F (about 38° C.) for 2 weeks (Exs. 7-64) for 1 month (Exs. 1-6 & 65-122)
		Interior	Shell	Beef Tallow	
1	0.80	9	6	8.5	clear
2	0.63	7.0	7	9.0	clear
3	0.83	6.0	6	9.0	clear
4	0.67	8.0	7	5.0	clear yellow
5A	0.73	5.0	8	7.0	slight haze
6	0.83	9.0	6	10.0	slight haze
7	0.70	6.1	5.0	6.8	clear
8	NT	NT	NT	NT	unstable
9	0.79	6.0	5.0	8.0	very hazy
10	0.79	6.0	7.0	7.0	clear
11	0.78	6.0	7.0	6.0	clear
12	0.80	7.0	6.5	8.0	slightly hazy
13	0.83	7.0	6.0	7.0	very slightly hazy
14	0.82	6.0	6.0	7.0	unstable
15	0.85	7.0	7.0	7.0	hazy
16	0.83	7.0	6.0	7.0	hazy
17	0.83	7.0	7.0	6.0	very slightly hazy
18	0.66	6.0	7.0	7.0	v.s. hazy
19	0.69	6.0	7.0	5.0	cle
20	0.67	7.0	7.0	6.0	cle
21	0.83	6.0	6.0	7.0	clear
22	0.68	7.0	7.5	8.0	hazy
23	0.74	6.0	7.5	7.0	very slightly hazy
24	0.72	8.0	6.5	8.0	hazy
25	0.69	7.5	6.5	9.0	unstable

Ex.	Drop Tests	Cleaning Test			Appearance at 100°F (about 38° C.) for 2 weeks (Exs. 7-64) for 1 month (Exs. 1-6 & 65-122)
		Interior	Shell	Beef Tallow	
26	0.74	8.5	6.5	8.0	unstable
27	0.71	6.0	6.5	9.0	clear
28	0.75	7.0	6.5	8.0	very hazy
29	0.68	6.0	6.5	7.0	unstable
30	0.71	6.0	4.0	5.5	clear
31	0.79	5.0	5.0	5.0	very slightly hazy
32	0.74	5.0	5.0	5.0	clear
33	0.77	6.0	5.0	4.5	very slightly hazy
34	0.88	5.0	4.0	4.0	clear
35	0.74	6.0	5.0	4.5	clear
36	0.77	6.0	6.0	4.5	clear
37	0.76	5.0	4.0	4.5	clear
38	0.73	6.0	3.0	4.0	clear
39	0.76	6.0	4.0	7.0	very slightly hazy
40	0.67	7.0	4.0	6.0	very slightly hazy
41	0.71	7.0	5.0	6.5	clear
42	0.68	6.0	4.0	6.5	clear
43	NT	6.0	3.0	4.0	unstable
44	NT	NT	NT	NT	unstable
45	NT	NT	NT	NT	unstable
46	0.70	6.0	5.0	5.0	clear
47	0.72	6.0	6.0	5.0	clear
48	0.69	6.0	5.0	6.0	clear
49	0.70	6.0	4.0	8.5	clear
50	0.73	6.0	5.5	6.5	clear
51	0.70	6.0	4.0	6.0	clear

Ex.	Drop Tests	Cleaning Test			Appearance at 100°F (about 38° C.) for 2 weeks (Exs. 7-64) for 1 month (Exs. 1-6 & 65-122)
		Interior	Shell	Beef Tallow	
52	0.71	5.5	5.2	6.0	clear
53	0.70	5.5	4.0	6.0	clear
54	0.69	5.5	5.0	4.5	clear
55	0.69	6.0	5.0	6.0	clear
56	0.58	6.0	5.0	6.0	clear
57	0.74	5.5	5.0	6.0	clear
58	0.73	5.0	4.5	4.5	clear
59	0.72	5.0	4.5	5.0	hazy
60	0.72	6.0	4.5	5.0	hazy
61	0.92	5.0	4.5	5.0	clear
62	0.74	5.0	4.5	5.0	clear
63	0.72	5.5	4.0	5.0	clear
64	0.67	6.0	4.5	5.5	clear
65	0.77	6.5	5.9	6.8	swirly
66	0.84	7.0	5.5	5.0	unstable
67	0.80	6.0	7.0	6.0	unstable
68	1.03	7.0	6.5	4.5	unstable
69	0.93	7.0	5.5	7.0	unstable
70	0.92	7.0	5.0	5.5	unstable
71	1.02	6.0	5.0	4.5	unstable
72	0.89	7.0	6.5	6.0	unstable
73	0.90	7.0	6.5	4.0	swirly/cloudy
74	0.84	7.0	6.5	6.0	unstable
75	0.78	6.0	6.5	6.0	slightly cloudy
76	0.81	7.0	8.0	5.0	cloudy
77	0.92	6.0	7.0	5.5	cloudy

-37-

Ex.	Drop Tests	Cleaning Test			Appearance at 100°F (about 38° C.) for 2 weeks (Exs. 7-64) for 1 month (Exs. 1-6 & 65-122)
		Interior	Shell	Beef Tallow	
78	0.89	8.0	7.0	7.5	unstable
79	0.86	6.0	6.5	5.5	unstable
80	0.86	8.0	7.0	5.5	unstable
81	0.79	6.0	7.0	6.5	unstable
82	0.93	7.0	7.0	5.0	unstable
83	0.76	7.0	7.0	6.5	swirly
84	0.88	8.0	7.0	5.0	unstable
85	0.90	7.0	7.0	4.5	unstable
86	0.67	6.0	7.0	6.0	slightly cloudy
87	0.76	6.5	5.0	8.0	slightly cloudy
88	0.77	6.0	4.5	7.0	swirly
89	0.71	NT	NT	NT	swirly
90	0.73	6.5	6.0	7.0	strands/swirly
91	0.73	6.0	5.0	8.0	clear
92	0.73	7.0	6.5	6.0	unstable
93	0.73	6.5	6.0	6.5	swirly
94	0.73	6.0	5.0	5.5	swirly
95	0.71	6.5	5.0	4.0	swirly
96	0.66	6.0	8.0	7.0	clear
97	0.75	7.0	4.5	8.0	unstable
98	0.75	6.5	4.8	7.0	strands/swirly
99	0.80	7.0	6.5	7.0	unstable
100	0.79	6.5	6.0	5.5	unstable
101	NT	NT	NT	NT	unstable
102	NT	NT	NT	NT	unstable
103	NT	NT	NT	NT	unstable

Ex.	Drop Tests	Cleaning Test			Appearance at 100°F (about 38° C.) for 2 weeks (Exs. 7-64) for 1 month (Exs. 1-6 & 65-122)
		Interior	Shell	Beef Tallow	
104	0.73	6.5	6.0	5.5	clear
105	0.76	7.0	6.0	7.0	unstable
106	0.75	6.5	6.0	6.0	swirly
107	0.74	7.0	6.5	6.5	swirly
108	0.74	6.5	6.5	6.5	swirly
109	0.75	6.5	8.0	6.0	swirly
110	0.73	6.5	5.5	6.0	unstable
111	0.74	6.5	4.5	7.0	slightly cloudy
112	0.71	6.5	6.5	7.0	swirly
113	0.75	6.5	6.5	6.0	oily/swirly
114	0.71	6.5	6.0	7.0	swirly
115	0.82	6.5	7.0	6.0	swirly
116	0.86	7.0	6.5	6.5	swirly
117	0.84	7.0	6.5	7.0	swirly
118	0.80	6.0	7.0	7.0	cloudy
119	0.70	6.0	6.8	7.5	unstable
120	NT	NT	NT	NT	unstable
121	0.79	6.5	5.0	6.5	clear
122	0.76	6.0	6.5	6.5	clear
NT - not tested					



Table 2

Example	Sliding Drop Test (3 drops)
1	4.5
2	4.5
3	4.5
4	3.0
5A	4.5
6	3.0
7	3.0
18	3.4
31	1.7
42	3.0
55	3.5
56	3.5
61	1.8
65	3-3.5
86	3.5-4.0
96	3.5-4.0

Many of the formulations of this invention remained stable, i.e., without a substantial white cloudy or strand like appearance in a clear solution, even after storage at 100°F for two weeks to a month. In general, the nonionic surfactants, and particularly the nonionic ethoxylated alcohols, tended to provide stable  
5 formulas. The amphoteric betaines, and particularly Lonzaine® CO (cocoamidopropyl betaine), also generally provided positive results. In addition, formulations using relatively long carbon chain amine oxides, such as Lonza Barlox®16-S and Lonza Barlox® 18-S in combination with a glycolic acid system were found to be quite stable.

10 The results of the water drop test set forth in Table 1 show that many of the formulations of this invention increased the hydrophobicity of the treated surface. Examples 2, 4, 18, 56, 86, 95, 96, 112 and 114 exhibited particularly strong hydrophobicity.

Notwithstanding a formulation's ability to deliver a protective silane coating  
15 and render a surface hydrophobic, the formulation should also have the ability to clean. The cleaning test results illustrated in Table 1, show that some of the formulations are particularly strong overall for each of the soil groups, while other formulations evidence strong cleaning properties for a particular soil group. Thus, the results of these tests indicate that the formulations of this invention are not only  
20 stable and provide a protective silane coating, but also provide effective cleaning efficacy, the scope of which can be modified depending on the nature of the formulation.

The results set forth in Table 2, also confirm that the formulations of Examples 1-7, 18, 42, 55, 56, 65, 86 and 96 rendered the surface of ceramic tiles  
25 treated with those formulations hydrophobic or water repellant.

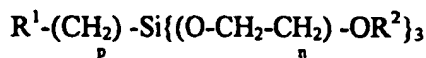
Industrial Applicability

The cleaning formulation of this invention are highly storage stable even when packaged in glass containers, and therefore conserve the active silane for  
5 attachment to treated surfaces. In addition, the method of applying the alkaline cleaning formulations of this invention may be advantageously used to clean and protect water covered surfaces with a minimal use of materials and effort.

Other variations and modifications of this invention will be obvious to those skilled in this art. This invention is not to be limited except as set forth in the  
10 following claims.

What Is Claimed Is:

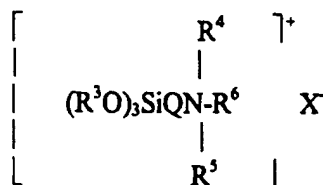
1. An acidic cleaning formulation for cleaning hard surfaces comprising:
  - (a) a surface modification agent selected from the group consisting of:
    - 5 (i) a hydrolyzed trialkoxysilane in an amount from about 0.00001 to about 10.0 percent by weight of said formulation and (ii) a hydrolyzable quaternary silane in an amount from about 0.00001 to about 10.0 percent by weight of the formulation;
    - (b) a surfactant in an amount from about 0.0001 to about 10.0 percent by
 10 weight of said formulation, provided that if the surface modification agent is a hydrolyzable quaternary silane then the surfactant is not a quaternary ammonium compound or a sulfobetaine;
    - (c) an alcohol having 1 to 12 carbon atoms; and
    - (d) water, wherein said formulation has a pH less than 7.0.
- 15 2. An acidic cleaning formulation according to claim 1, wherein said hydrolyzed trialkoxysilane is formed in an aqueous emulsion from a hydrolyzable trialkoxysilane compound emulsified in water with about 5 to 100 percent by weight of an emulsifier based on the weight of the hydrolyzable trialkoxysilane.
- 20 3. An acidic cleaning formulation according to claim 2, wherein said hydrolyzable trialkoxysilane is represented by formula (I):



- 25 wherein R<sup>1</sup> is selected from the group consisting of a perfluoroalkyl group of 3 to 18 carbon atoms or an alkyl group of 3 to 24 carbon atoms, each R<sup>2</sup> is independently an alkyl group having 1 to 3 carbon atoms, p is 0 to 4 and n is 2 to 10.

-43-

4. An acidic cleaning formulation according to claim 3, wherein said emulsifier is an ethoxylated C<sub>8-18</sub> amine salt.
5. An acidic cleaning formulation according to claim 1, wherein said surfactant is selected from the group consisting of nonionic surfactants, amphoteric betaines, amphoteric sultaines, imidazoline amphoterics, amine oxides, quaternary cationics, dialkoxyl alkyl quaternaries and mixtures thereof.
6. An acidic cleaning formulation according to claim 1, wherein said alcohol is selected from the group consisting of mono-hydric alcohols, di-hydric alcohols, tri-hydric alcohols and mixtures thereof.
7. An acidic cleaning formulation according to claim 1, further comprising an acid in an amount effective to provide said formulation with a pH less than 7.0, wherein said acid is selected from the group consisting of glycolic acid, lactic acid, citric acid, gluconic acid, sulfamic acid and acetic acid.
8. An acidic cleaning formulation according to claim 1, wherein the pH of said formulation is about 0.5 to about 6.95.
9. An acidic cleaning formulation according to claim 1, further comprising a siloxane in an amount effective to reduce autophobicity of the cleaning formulation.



10. An acidic cleaning formulation according to claim 1, wherein said surface modification agent is a hydrolyzable quaternary silane represented by the formula

wherein  $R^3$  is a hydrolyzable lower alkyl group having 1 to 6 carbon atoms,  $R^4$ ,  $R^5$  and  $R^6$  are each independently alkyl groups having 1 to 24 carbon atoms, Q is an alkylene radical having 1 to 6 carbon atoms and X is an alkali metal.

5

11. An acidic cleaning formulation according to claim 10, wherein said hydrolyzable quaternary silane is selected from the group consisting of 3-(trimethoxysilyl) propyldimethyloctadecylammonium chloride and 3-(trimethoxysilylpropyl) didecylmethylammonium chloride.

10

12. An acidic cleaning formulation for cleaning hard surfaces comprising:

(i) a hydrolyzed trialkoxysilane in an amount from about 0.00001 to about 10 percent by weight of said formulation, wherein said hydrolyzed trialkoxysilane is formed in an aqueous emulsion from a  $C_{18}$ -alkyltrialkoxysilane compound  
15 emulsified in water with a  $C_{8-18}$  tetraalkylammonium chloride in an amount of about 30 to 50 percent by weight of the silane;

(ii) a surfactant in an amount from about 0.00001 to about 10.0 percent by weight of said formulation, wherein said surfactant is selected from the group consisting of amine oxides, amphoteric sultaines, amphoteric betaines, nonionic  
20 surfactants and mixtures thereof;

(iii) at least one mono-hydric alcohol, di-hydric alcohol, or tri-hydric alcohol;

(iv) optionally, at least one glycol ether;

(v) an acid in an amount effective so that said formulation has a pH  
25 between about 0.5 and about 6.95; and

(vi) water.

13. An acidic cleaning formulation according to claim 12, wherein said mono-hydric alcohol, di-hydric alcohol or tri-hydric alcohol is selected from the group  
30 consisting of isopropanol, hexanol and mixtures thereof.

14. An acidic cleaning formulation according to claim 13, wherein said glycol ether is a mixture of propylene glycol n-butyl ether, propylene glycol n-propyl ether and dipropylene glycol methyl ether.
- 5 15. A method for cleaning and modifying a hard surface covered by water comprising the step of applying an acidic cleaning formulation according to claim 1, to water contacting said hard surface in an amount effective to modify said hard surface by attachment of said surface modification agent to said surface.
- 10 16. A method according to claim 15, wherein the concentration of said hydrolyzed trialkoxysilane in said water is from about 0.10 to about 10,000 ppm.

## INTERNATIONAL SEARCH REPORT

Intern. Appl. Application No

PCT/US 97/05191

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 C11D3/16 C11D3/43

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 92 14810 A (JOHNSON & SON INC S C) 3 September 1992 cited in the application see page 22, paragraph 1; examples 8,10,31,33 ---	1,5,7,8, 10,11,15
X	US 4 005 028 A (HECKERT DAVID C ET AL) 25 January 1977  see claims 1,3,6; example XIII see column 22, line 32 - line 42 see column 22, line 60 - line 68 see column 27, line 38 - line 45 ---	1,6,8, 10,11, 15,16
A	US 4 859 359 A (DEMATTEO JOHN A ET AL) 22 August 1989 cited in the application see claims; examples ---	1,6,7
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*A\* document member of the same patent family

Date of the actual completion of the international search

18 July 1997

Date of mailing of the international search report

25.07.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax (+31-70) 340-3016

Authorized officer

Loiselet-Taisne, S



## INTERNATIONAL SEARCH REPORT

Internat. Application No  
PCT/US 97/05191

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 23804 A (DU PONT) 8 September 1995 cited in the application see page 7, line 18 - line 19; claims; examples ---	1-4
A	EP 0 279 623 A (DOW CORNING) 24 August 1988 see page 5, line 2 - line 9 see page 6, line 2 - line 14 see page 12, line 41 - line 65 ---	1
A	US 3 249 550 A (N.T. METTERS) 3 May 1966 see claims; examples -----	1

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/05191

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9214810 A	03-09-92	AU 655621 B AU 9144691 A CA 2100670 A,C EP 0640122 A JP 6505036 T KR 9615974 B US 5411585 A	05-01-95 15-09-92 16-08-92 01-03-95 09-06-94 25-11-96 02-05-95
US 4005028 A	25-01-77	NONE	
US 4859359 A	22-08-89	NONE	
WO 9523804 A	08-09-95	US 5550184 A AU 1937695 A EP 0748323 A US 5552476 A	27-08-96 18-09-95 18-12-96 03-09-96
EP 0279623 A	24-08-88	US 4842766 A AU 595983 B AU 1190688 A CA 1309314 A DE 3882246 A DE 3882246 T JP 63232837 A KR 9610077 B	27-06-89 12-04-90 18-08-88 27-10-92 19-08-93 03-02-94 28-09-88 25-07-96
US 3249550 A	03-05-66	NONE	